Trabajo de grado

(Proyecto de investigación)

Facultad de Ciencias Naturales y Exactas

Universidad del Valle

Solving Dirac equation for H_2^+ using B-splines

By:
Mario A. Henao Ayala

Advisor:
Prof. Javier Madroñero

Co-advisor:
Dr. Beatriz Londoño

Santiago de Cali, Septiembre 2 del 2016

Contents

Abstract iii

Resumen v

Introduction 1

1 Dirac equation for H_2^+ 3

1.1 Dirac equation formalism . . . 3

1.1.1 Derivation of *Dirac equation* . . . 3

1.1.2 Comments on the positivity of probability . . . 4

1.1.3 Dirac matrices . . . 4

1.2 Methodology . . . 5

1.2.1 Dirac equation for H_2^+ in elliptic coordinates . . . 5

1.2.2 Reducing one dimension of the problem . . . 6

2 Numerical implementation of Dirac Equation for H_2^+ in elliptic coordinates 9

2.1 B-splines as a basis set . . . 9

2.1.1 General aspects of the B-splines . . . 9

2.2 Code description . . . 11

2.3 Example: Yukawa potential . . . 13

2.4 Discussion on convergence . . . 13

2.4.1 Dilation transformation . . . 14

2.4.2 Preliminary results . . . 14

3 Summary and outlook 17

A Dirac Equation for H_2^+ 19

Abstract

Controlled formation of molecules in the ground state has represented a challenge. Nevertheless, there has been important advances in this direction in molecular physics and chemistry due to its variety of applications, specially for being good candidates for quantum simulators. Photoassociation is a technique developed to achieve this task starting from ultracold gases of atoms and carefully carrying it to a molecular system in the ground state. This technique has been proved to be enhanced via spin-orbit couplings in the system. Due to this, it is important to understand from a relativistic point of view the behavior of molecular systems.

In this work we present a numerical approach to the solution of the *Dirac equation* for the H_2^+ molecule. In the first chapter we show the methodology used to reduce the problem to a *generalized eigenvalue problem*. In the second chapter we describe the numerical implementation which is finally used to calculate the ground state energy for the system and we discuss on the convergence of the results obtained.

Resumen

La formación controlada de moléculas en el estado base ha representado un desafío, pero al tiempo también ha habido importantes avances en esta dirección en física molecular y química debido a su variedad de aplicaciones, en especial por ser buenos candidatos para ser simuladores cuánticos. La foto-asociación es una técnica desarrollada para cumplir esta tarea empezando desde un gas de átomos ultrafríos y llevándolos cuidadosamente hasta el estado base de un sistema molecular. Se ha probado que esta técnica se ve favorecida por el acople espín-órbita presente en el sistema. Debido a esto es importante entender los sistemas moleculares desde una perspectiva relativista.

En este trabajo presentamos un acercamiento numérico a las solución de la *ecuación de Dirac* para la molécula de H_2^+. En el primer capítulo mostramos la metodología utilizada para llevar el problema a un *problema de valores propios generalizado*. En el segundo capítulo describimos la implementación numérica que finalmente es usada para calcular la energía del estado base de este sistema y discutimos sobre la convergencia de los resultados obtenidos.

Introduction

Photo-association of cold atoms has been the first successful approach to form molecules in the ground state at temperatures in the order of micro-Kelvin. The major challenge to the formation of these molecules is to take the long distances between atoms in an ultracold gas to the typical distances of a molecular bond in the ground state [1]. The energy level structure and the ro-vibrational wave functions of alkali dimers, when we take into account heavy atoms, is drastically changed due to *spin-orbit coupling*. This coupling is the responsible of phenomena that enhances photo-association such as excited electronic molecular potentials with double well structure and resonant couplings between electronic states [2].

Perturbative approaches to the *spin-orbit coupling* take us to approximate functions that in general have to be adjusted to the experimental data of the specific molecule studied. Several works treat the problem by starting from *Schrödinger equation* and introducing *spin-orbit coupling* as a perturbation to the Hamiltonian [1–5].

High resolution spectroscopy, thank to photo-association of cold atoms, has revealed the important role of *spin-orbit coupling* [6], in particular to enhance the photo-association process [1–3].

Molecular potentials corresponding to excited electronic states exhibits interesting properties on creating molecules in the ground state, the majority of examples in the literature come from creation of double well potentials and resonant coupling of two electronic states, and both phenomena are present in heavy alkali dimers due to its strong *spin-orbit coupling* [3–5].

Rigorous calculations [5, 7] study this *spin-orbit* interaction starting from *Schrödinger equation* as mentioned before. However, solving *Dirac equation* for heavy molecules is a difficult task. In this work we propose an approach to this problem, that is solving *Dirac equation* for the simplest possible molecule which is H_2^+ to start the understanding of this coupling from a more fundamental point of view.

We use a basis, called B-splines, introduced by Schoenberg in 1946 [8] and already successfully used in several atomic and molecular systems showing good results in both bound and continuum states [9–13] not only for *Schrödinger equation* but also for *Dirac equation*.

In Chapter 1 we discuss the formalism of *Dirac equation* together with some definitions and properties of quantities of physical interest. Then we expose a coordinate system useful to reduce the problem of the H_2^+ molecule to 4 coupled differential equations due to a symmetry related to the conservation of the z-component of the total angular momentum of the electron; this problem can be transformed into a *generalized eigenvalue problem*. In Chapter 2 we present the procedure used to solve numerically the *generalized eigenvalue problem* presented in the previous chapter. First we present some important properties of *B-splines*, then we describe the numerical method

to find the eigenvalues for the H_2^+ molecule, showing an example of a previous version of the program to solve the 1-dimensional *Screened hydrogen atom, (Yukawa potential)*, and finally we show some preliminary results on the ground state energies of this molecule and discuss on the convergence. In Chapter 3 we give some conclusions and perspectives of this work.

Chapter 1

Dirac equation for H_2^+

Knowing that the *spin-orbit coupling* is an merely relativistic effect, it is important to consider the problem under the Dirac formalism to have a more fundamental idea about this interaction in specific. In this section we will explain in brief the Dirac equation formalism and we will explain the methodology used to reduce the initial problem for the the H_2^+ molecule to a 2-dimensional system of 4 coupled differential equations.

1.1 Dirac equation formalism

1.1.1 Derivation of *Dirac equation*

The idea behind the *Dirac equation* is basically to construct a equation able to describe the behavior of a *spin*-$1/2$ particle in the framework of *Special Relativity* [14], introduced by P.A.M Dirac in 1929. We claim that solutions of that equation must satisfy the *Einstein relation* for energy

$$E^2 = p^2c^2 + m^2c^4, \tag{1.1}$$

where p and m are the momentum and mass of the particle, respectively, and c is the speed of the light.

In order to have a positive *density* (built from the wave function), we need to consider a differential equation of first order, in contrast to *Klein-Gordon equation*. The requirement of relativistic covariance demands that the spatial derivatives may only be of first order too [15], in atomic units that is

$$i\frac{\partial\bar{\phi}}{\partial t} = [c\alpha^k p_k + \beta mc^2]\bar{\phi} = \left[\frac{c}{i}\alpha^k\partial_k + \beta mc^2\right]\bar{\phi} \equiv H\bar{\phi}. \tag{1.2}$$

As we can see the Hamiltonian H is linear in the rest energy and in momentum but the coefficients α^k and β can not be just numbers because they will not satisfy (1.1), thus they have to be $N \times N$ matrices and $\bar{\phi}$ is necessarily an N-component quantity.

We also need (1.2) to be Lorentz covariant and there exist a conserved 4-current whose time component is a positive density.

Acting two times the hamiltonian on a wave function $\bar{\phi}$ and comparing this to the *Klein-Gordon equation* we can see that the matrices must satisfy the following relationships

$$\alpha^i\alpha^j + \alpha^j\alpha^i = 2\delta^{ij}\mathbb{I}, \quad \alpha^i\beta + \beta\alpha^i = 0, \quad (\alpha^i)^2 = \beta^2 = \mathbb{I}. \tag{1.3}$$

1.1.2 Comments on the positivity of probability

Writing the adjoint to $\bar{\phi}$ as

$$\bar{\phi}^\dagger = (\bar{\phi}_1^*, ..., \bar{\phi}_N^*), \tag{1.4}$$

and multiplying it to (1.2) we can build a continuity equation, if and only if the matrices α^i and β are hermitian, i.e.,

$$(\alpha^i)^\dagger = \alpha^i, \quad \beta^\dagger = \beta. \tag{1.5}$$

The quantity that fulfills this continuity equation is the *density* defined by

$$\rho \equiv \bar{\phi}^\dagger\bar{\phi} = \sum_{\alpha=1}^{N} \bar{\phi}_\alpha^*\bar{\phi}_\alpha \tag{1.6}$$

and the *current density*

$$j^k \equiv c\bar{\phi}^\dagger\alpha^k\bar{\phi}, \tag{1.7}$$

with temporal component $j^0 \equiv c\rho$, which is positive definite, and can be interpreted as a probability density [15].

1.1.3 Dirac matrices

According to (1.3) these matrices possess only eigenvalues ± 1; also they are traceless

$$\mathrm{Tr}\alpha^{\mathrm{k}} = \mathrm{Tr}\beta = 0, \tag{1.8}$$

then we can say that at least that N is even. Finally it can be proven that the smallest N possible to realize the algebraic structure in (1.3) is 4 [15].

A particular representation of the *Dirac matrices* is

$$\alpha^i = \begin{pmatrix} 0 & \sigma^i \\ \sigma^i & 0 \end{pmatrix}, \quad \beta = \begin{pmatrix} \mathbb{I} & 0 \\ 0 & \mathbb{I} \end{pmatrix}, \tag{1.9}$$

that together with (1.2) is referred to as the *standard representation* of the *Dirac equation*; the quantity $\bar{\phi}$ is called a 4-spinor, or *Dirac spinor* [15].

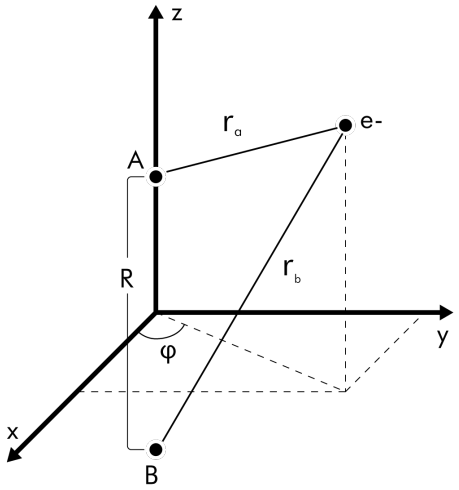

Figure 1.1: diagram for H_2^+ molecule, nuclei A and B lay on z-axis

1.2 Methodology

1.2.1 Dirac equation for H_2^+ in elliptic coordinates

When we have systems like H_2^+ where there is no more spherical symmetry, due to the two nuclei interacting with the electron, it is useful to solve the problem in *elliptic coordinates* defined by

$$\rho := \frac{r_\mathrm{a} + r_\mathrm{b}}{R}, \quad \tau := \frac{r_\mathrm{a} - r_\mathrm{b}}{R}, \quad \varphi := \text{usual polar angle}, \tag{1.10}$$

where $r_{\mathrm{a,b}}$ and φ are shown in Fig. 1.1 and the ranges of these variables are $1 \leq \rho < \infty$, $-1 \leq \tau \leq 1$ and $0 < \varphi \leq 2\pi$.

Their relation to Cartesian coordinates are

$$x = \frac{R}{2}\cos\varphi\sqrt{(\rho^2-1)(1-\tau^2)}, \quad y = \frac{R}{2}\sin\varphi\sqrt{(\rho^2-1)(1-\tau^2)}, \quad z = -\frac{R\rho\tau}{2}. \tag{1.11}$$

In general, using atomic units, the potential energy for diatomic molecules is the sum of individual *Coulomb Potentials*

$$V = -\frac{Z_\mathrm{a}e^2}{r_\mathrm{a}} - \frac{Z_\mathrm{b}e^2}{r_\mathrm{b}}, \tag{1.12}$$

where $Z_{\mathrm{a,b}}$ are the atomic charge for each nucleus in the molecule

In the case of H_2^+ we have $Z_\mathrm{a} = Z_\mathrm{b} =: Z$, therefore,

$$V(\rho,\tau) = \frac{Ze^2}{R}\left(\frac{-4\rho}{\rho^2-\tau^2}\right). \tag{1.13}$$

We know that the Dirac equation in general form reads

$$\bar{E}\begin{pmatrix}\bar{\phi}_1\\ \bar{\phi}_2\\ \bar{\phi}_3\\ \bar{\phi}_4\end{pmatrix} = \begin{pmatrix} V+mc^2 & 0 & p_z & p_x-ip_y \\ 0 & V+mc^2 & p_x+ip_y & -p_z \\ p_z & p_x-ip_y & V-mc^2 & 0 \\ p_x+ip_y & -p_z & 0 & V-mc^2 \end{pmatrix}\begin{pmatrix}\bar{\phi}_1\\ \bar{\phi}_2\\ \bar{\phi}_3\\ \bar{\phi}_4\end{pmatrix}. \tag{1.14}$$

1.2.2 Reducing one dimension of the problem

Using (1.11) we can calculate each of the momentum operators in terms of the elliptic coordinates. Since p_z does not depend on φ it is possible to use the *Ansatz* [16]

$$\bar{\phi}_k(\rho,\tau,\varphi) = \phi_k(\rho,\tau)e^{i(\mu-1/2+\lambda_k)\varphi}, \tag{1.15}$$

which is a consequence of the conservation of the projection to the z-axis of the total angular momentum of the electron due to the cylindrical symmetry of the problem. Here $\lambda_k = (0,1,0,1)$ for $k = (1,2,3,4)$ and μ is the projection on the z-axis of the total angular momentum of the electron. This *Ansatz* let us to eliminate the coordinate φ from our equations and we get a two-dimensional system of four coupled differential equations that look like

$$\bar{E}\phi_1 = \bar{A}_+\phi_1 + \bar{B}\phi_3 + \bar{C}_+\phi_4, \tag{1.16}$$

$$\bar{E}\phi_2 = \bar{A}_+\phi_2 - \bar{B}\phi_4 + \bar{C}_-\phi_3, \tag{1.17}$$

$$\bar{E}\phi_3 = \bar{A}_-\phi_3 + \bar{B}\phi_1 + \bar{C}_+\phi_2, \tag{1.18}$$

$$\bar{E}\phi_4 = \bar{A}_-\phi_4 - \bar{B}\phi_2 + \bar{C}_-\phi_1, \tag{1.19}$$

where $\bar{A}_\pm, \bar{B}, \bar{C}_\pm$ are first order differential operators in the coordinates ρ and τ defined by the following expressions (see the details in App. A)

$$\begin{aligned}\bar{A}_\pm &:= \left[\frac{Ze^2}{R}\left(\frac{-4\rho}{\rho^2-\tau^2}\right) \pm mc^2)\right], \quad \bar{B} := -i\frac{2\hbar}{R}\frac{1}{\rho^2-\tau^2}\left[(1-\rho^2)\tau\frac{\partial}{\partial\rho} + (\tau^2-1)\rho\frac{\partial}{\partial\tau}\right], \\ \bar{C}_\pm &:= i\frac{2\hbar}{R}\left[\frac{(\mu\pm 1/2)}{[(\rho^2-1)(1-\tau^2)]^{1/2}} - \frac{[(\rho^2-1)(1-\tau^2)]^{1/2}}{\rho^2-\tau^2}\left(\rho\frac{\partial}{\partial\rho} - \tau\frac{\partial}{\partial\tau}\right)\right],\end{aligned} \tag{1.20}$$

At this point what we have is a sort of *eigenvalue problem* if we write the problem in matrix form

$$\bar{E}\begin{pmatrix}\phi_1\\ \phi_2\\ \phi_3\\ \phi_4\end{pmatrix} = \begin{pmatrix} \bar{A}_+ & 0 & \bar{B} & \bar{C}_+ \\ 0 & \bar{A}_+ & \bar{C}_- & \bar{B}^* \\ \bar{B} & \bar{C}_+ & \bar{A}_- & 0 \\ \bar{C}_- & \bar{B}^* & 0 & \bar{A}_- \end{pmatrix}\begin{pmatrix}\phi_1\\ \phi_2\\ \phi_3\\ \phi_4\end{pmatrix}. \tag{1.21}$$

In the next chapter we will show that the representation of (1.21) in a *B-spline* basis leads to a *generalized eigenvalue problem*. We point out that the transformation (1.15) is non-unitary. Therefore, the *generalized eigenvalue problem* is not anymore hermitian and its eigenvalues are in general complex. As we will see in Sec. 2.4.2 the ground state is real.

Chapter 2

Numerical implementation of Dirac Equation for H_2^+ in elliptic coordinates

In this section we will discuss some general and important properties of the basis functions we used to expand our matrices and wave functions called B-splines in order to diagonalize the problem depicted in the previous section. We also explain how the computational process works in an schematic way and finally we comment on some preliminary results for the ground state energies of the H_2^+ molecule.

2.1 B-splines as a basis set

From the computational point of view it is important to use a numerical stable basis to calculate physical quantities; The spline bases, or *B-splines* is a basis that has demonstrated good approximations solving both Schrödinger [10,11] and Dirac [12,13] equations. It is a basis set introduced by Schoenberg in 1946 [8] and later summarized by de Boor [17]. This basis has some properties that are useful for numerical calculations that we will see in a moment.

2.1.1 General aspects of the B-splines

It is necessary to introduce a partition of an interval, called *box*, to be able to define what a B-spline basis is. Let us consider an interval $I = [a, b]$ divided into l subintervals $I_j = [x_j, x_{j+1}]$ such that,

$$a = x_1 < x_2 < \cdots < x_{l+1} = b. \tag{2.1}$$

The set of points $\{x_j\}$ are called *breakpoints* (bps).

A *B-spline* is a *piecewise polynomial function* (pp-function) over $[a, b]$ of order k [1], which usually provides a good approximation of wavefunctions in a rather easy way.

[1] That is, a function which restricted to each interval I_j is a polynomial of maximum degree $k - 1$

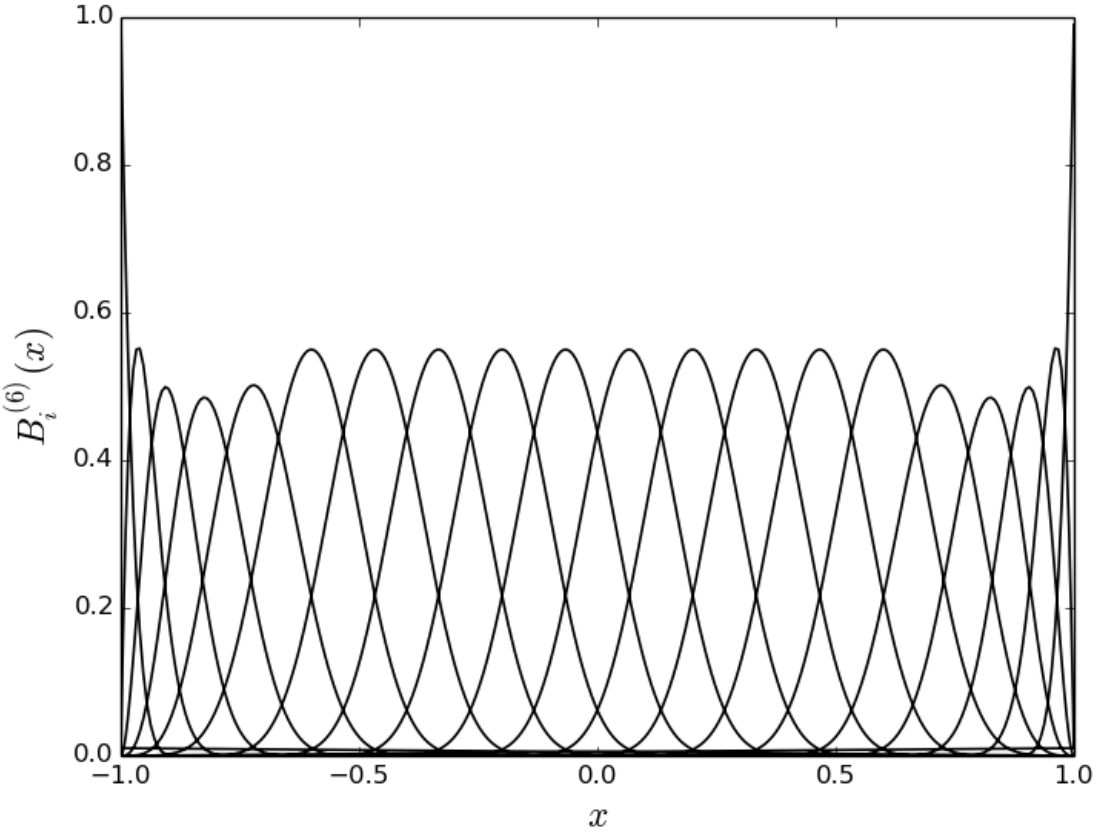

Figure 2.1: Complete set of 20 B-splines of order 6 in a box $[-1, 1]$ with a equally spaced sequence of bps

B-splines can be constructed recursively in the following way:

The B-spline functions of lowest order $(k = 1)$ are step functions of the form

$$B_i^1(x) = \begin{cases} 1 & x_i \leq x < x_{i+1} \\ 0 & \text{otherwise} \end{cases} \tag{2.2}$$

and the higher order B-splines constructed from the recursion relation [17, 18]

$$B_i^k(x) = \frac{x - x_i}{x_{i+k-1} - x_i} B_i^{k-1}(x) + \frac{x_{i+k} - x}{x_{i+k} - x_{i+1}} B_{i+1}^{k-1}(x), \tag{2.3}$$

In Fig. 2.1 we plot the set of B-splines of order $k = 6$, in a box $[-1, 1]$ with a equally spaced sequence of bps.

Some useful properties of these functions are listed bellow and can be visualized in Fig. 2.1

1. $B_i(x)$ is a pp-function of order k over $[x_i, x_{i+k}]$.

2. $B_i(x) > 0$ for $x \in]x_i, x_{i+k}[$ and zero elsewhere.

3. $B_i(x)B_j(x) = 0$ for $\mid i - j \mid \geq k$. This property tells us that exactly k B-splines are nonzero over $]x_i, x_{i+k}[$ which is numerically very useful because matrices built with B-splines (overlap, hamiltonian, etc) are exactly k-banded.

4. Normalization property: $\sum_i B_i(x) = 1$ over all the box.

The definitions (2.2) and (2.3) shows that B-spline functions of order k are indeed pp-functions of maximum degree $k-1$ and they provide us an algorithm to calculate the value of a B-spline at x starting from the B-spline of order 1. In the numerical calculations we used `FORTRAN` routines developed by de Boor [17] such that `BSPLVP` to evaluate all k B-splines that are nonzero and its derivatives at a certain x given the order k, the knot sequence $\{x_j\}$, and the index of the left-closest knot to x.

The Dirac equation involves derivatives of first order. Therefore, we will also need to calculate derivatives of B-splines. The derivative of a B-spline of order k is also a pp-function of order $k-1$ which can be computed from (2.3):

$$\frac{dB_i^k(x)}{dx} = \frac{k-1}{x_{i+k-1} - x_i} B_i^{k-1}(x) - \frac{k-1}{x_{i+k} - x_{i+1}} B_{i+1}^{k-1}(x). \tag{2.4}$$

We thus use the same subroutine `BSPLVP` to evaluate these derivatives by changing the spline order $(k \to k-1)$.

2.2 Code description

We prepare, separately, each B-spline basis for ρ and τ using the routines `BSPLVP` [17] in the boxes $[1, \rho_{\max}]$ and $[-1, 1]$ respectively. Since our problem is to diagonalize the matrix in (1.21) each component of the vector ϕ_k can be expanded in the following way

$$\phi_k(\rho, \tau) = \sum_{i_\rho=1}^{n_\rho} \sum_{i_\tau=1}^{n_\tau} C_{i_\rho i_\tau}^k B_{i_\rho}(\rho) B_{i_\tau}(\tau) \tag{2.5}$$

where $B_{i_\rho}(\rho), B_{i_\tau}(\tau)$ are B-spline functions of a certain order and i_ρ, i_τ are the indices in the box used to each coordinate ρ, τ respectively, and n_ρ, n_τ are the total number of B-splines used to expand each component of the *Dirac spinor* in its respective directions.

Then we have to find the matrix representation in the B-spline basis of each operator in (1.20); we have to keep in mind that the right-hand side of (1.21) turns into an *overlap matrix* $\boldsymbol{S}$ because B-splines are not orthogonal, that is

$$S_{ij} = \langle B_{i_\rho}(\rho) B_{i_\tau}(\tau) \mid B_{j_\rho}(\rho) B_{j_\tau}(\tau) \rangle. \tag{2.6}$$

Here, i, j are indices that keep a relationship with the B-spline indices i_ρ, i_τ, according to the specific storage of the matrix elements used. Due to the fact that our problem is 2-dimensional the matrices built with this B-spline basis are almost block-banded matrices, see Fig. 2.2.

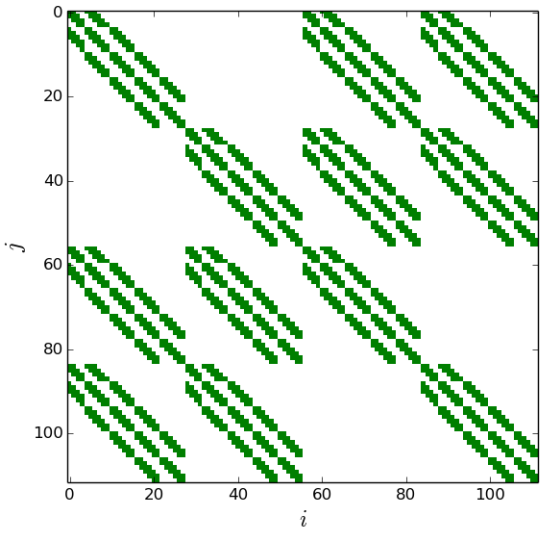

Figure 2.2: Matrix structure for the right-hand matrix in (1.21) for a small basis of 6 elements in each direction ρ and τ of order 2. We used the natural way to storage the elements of the matrix, where $i = 1, 2, ..., 4n_\rho n_\tau$ corresponds to pairs of indices $i_\rho i_\tau = 11, 12, ..., 1n_\tau, 21, 22, ..., 2n_\tau, ..., n_\rho 1, n_\rho 2, ..., n_\rho n_\tau$ and the same for j; and then we apply the boundary conditions mentioned after. In this particular basis the matrix has three 3-bands in each block.

It is important to remember that the boundary conditions are present in what we may think are ill-defined points in (1.20), for instance the positions $(\rho, \tau) = (1, -1)$ and $(\rho, \tau) = (1, 1)$ are exactly the positions of nuclei A and B respectively in the H_2^+ molecule. For numerical purposes we lift these divergences by multiplying (1.21) by $\bar{D} := [(\rho^2 - 1)(1 - \tau^2)]^{1/2}(\rho^2 - \tau^2)$. The other boundary conditions are

$$\phi_k(\rho_{\max}, \tau) = 0 \tag{2.7}$$

for each k, because we are interested in bound states of the problem. Since the only B-spline that is nonzero in $\rho_{\max}$ is B_{n_ρ}, see Fig. 2.1, we have

$$\phi_k(\rho_{\max}, \tau) = \sum_{i_\tau=1}^{n_\tau} C^k_{n_\rho i_\tau} B_{n_\rho}(\rho_{\max}) B_{i_\tau}(\tau) = 0, \tag{2.8}$$

which lead us to n_τ conditions for each component of the *Dirac spinor*.

Once the matrices are built we use a `LAPACK` subroutine called `ZGGEV` to find the *eigenvalues* of the *generalized eigenvalue problem*.

Table 2.1: Eigenvalues $E(\lambda)$ for the first two levels on the hydrogen atom with a Yukawa potential for $l = 0$, in atomic units.

λ	$E_1(\lambda)$	λ	$E_2(\lambda)$
0.1	-0.4070580306134	0.01	-0.1152932851679
0.2	-0.3268085113691	0.02	-0.1061483202446
0.3	-0.2576385863030	0.03	-0.0975317861346
0.4	-0.1983760833618	0.04	-0.0894146341851
0.5	-0.1481170218899	0.05	-0.0817711957952
0.6	-0.1061359075058	0.06	-0.0745785344127
0.7	-0.0718335559045	0.07	-0.0678159599814
0.8	-0.0447043044973	0.08	-0.0614646562123
0.9	-0.0243141938274	0.09	-0.0555073885532

2.3 Example: Yukawa potential

The procedure explained before is a generalization of a previous code developed by us to solve the 1-dimensional *Schrödinger equation* in presence of the *Yukawa potential*, or *Screened hydrogen atom*, where

$$V_{\text{eff}}(r) = -\frac{Ze^{-\lambda r}}{r} + \frac{l(l+1)}{2r^2} \tag{2.9}$$

here, l is the angular momentum quantum number of the electron and λ is called the screen parameter.

The structure of the code is exactly the same but here it is much simpler because we need to build just one B-spline basis and our wave function is a scalar function. Also the operators we have to represent in matrices are the *effective potential*, *kinetic energy* and the *overlap*. Finally we use a *Lanczos algorithm* [19–22] to diagonalize our problem and thus find the energies of the system.

We used a basis of $n = 351$ B-splines of order $k = 8$ in a box $[0, 100]$ with a equally spaced knot sequence and a screen parameter λ changing from 0.01 to 0.9. In Tab. 2.1 we show our results for the first two energy levels for $l = 0$ and several values of the parameter λ. We write down there the converged significant digits which coincide with the results reported in [23].

2.4 Discussion on convergence

In contrast to the *Yukawa problem* for the H_2^+ molecule we need to expand 4 wave functions in 2 different directions ρ and τ which leads us to a $(4n_\rho n_\tau - 4n_\tau - 8) \times (4n_\rho n_\tau - 4n_\tau - 8)$ matrix to diagonalize. Thus, the biggest basis that we could use was obtained for $n_\rho = n_\tau = 80$ which leads us to a $25\,272 \times 25\,272$ matrix which requires 10 GB of storage space. Including the overlap matrix and working space for the `LAPACK` subroutines our code requires approximately 40 GB of RAM which rounds the limit of our computer resources. It is worth to mention that this number of basis functions is small compared with the one used *Yukawa problem*.

2.4.1 Dilation transformation

We have to keep in mind that the equation we are solving is a relativistic problem, that is the eigenvalues we are looking for are, in atomic units,

$$E = c^2 + \epsilon \tag{2.10}$$

and for atomic and molecular systems the term $c^2 \approx 18778.8624182$ is way bigger than ϵ so we used a *unitarity transformation* to the Hamiltonian to avoid ill conditioned matrices. Our Hamiltonian has three terms $c\boldsymbol{\alpha}\cdot\boldsymbol{p}$, βmc^2 and the potential $V(\boldsymbol{r}) \propto -\dfrac{1}{r_\mathrm{a}} - \dfrac{1}{r_\mathrm{b}}$; according to what we said before these three terms are of different orders of magnitude so we can apply a *dilation transformation*, mediated by the dilation unitary operator [24]

$$D_\theta = \exp\left(\mathrm{i}\theta\frac{\boldsymbol{r}\cdot\boldsymbol{p} + \boldsymbol{p}\cdot\boldsymbol{r}}{2}\right) \tag{2.11}$$

and defining $\theta = \log\gamma$ effectively results in the transformation of position and momentum operators according to

$$\boldsymbol{r} \to \gamma\boldsymbol{r}, \quad \boldsymbol{p} \to \frac{\boldsymbol{p}}{\gamma}. \tag{2.12}$$

The unitarity of this transformation guarantees that the eigenvalues are unchanged. However, as a consequence of the truncation of the basis, leading to a finite matrix representation, there is a numerically induced dependence. Therefore, γ can be used as an effective variational parameter.

2.4.2 Preliminary results

We did a plenty number of calculations for the ground state energy of the H_2^+ molecule varying the number of B-splines n_ρ, n_τ used in each direction, the order of these functions k_ρ, k_τ, the maximum value ρ_max and the dilation parameter γ and we show in the following tables the results obtained.

The *Ansatz* (1.15) leads to a non-hermitian *generalized eigenvalue problem* with complex eigenvalues. A typical (positive energy) spectrum is shown in Fig. 2.3. However, the ground state (with lowest positive energy) exhibits an effectively zero imaginary part. Indeed, the absolute value of its imaginary part is less than 10^{-11} atomic units in all our calculations. In Tab. 2.2 we show the ground state eigenvalue as a function of the box size ρ_max, the number of B-splines n and their order k for $\gamma = 1/c$, being $c = 137.0359895$ the speed of light.

From Tab. 2.2 we also obtain that the optimal value for the box size ρ_max, among the possible values our computer resources allow us to explore, is near 250. For this value we performed more calculations for different values of the dilation parameter γ as shown in Tab. 2.3.

The results presented in Tab. 2.3 still exhibit a dependence on the box size, and therefore, on the basis size. We cannot conclude that they are converged. Indeed, a direct comparison with other calculations (see Refs. [25, 26]), where the obtained energy of the ground state is $E = 18777.76$, confirms this observation. We observe that increasing the size of the basis improves

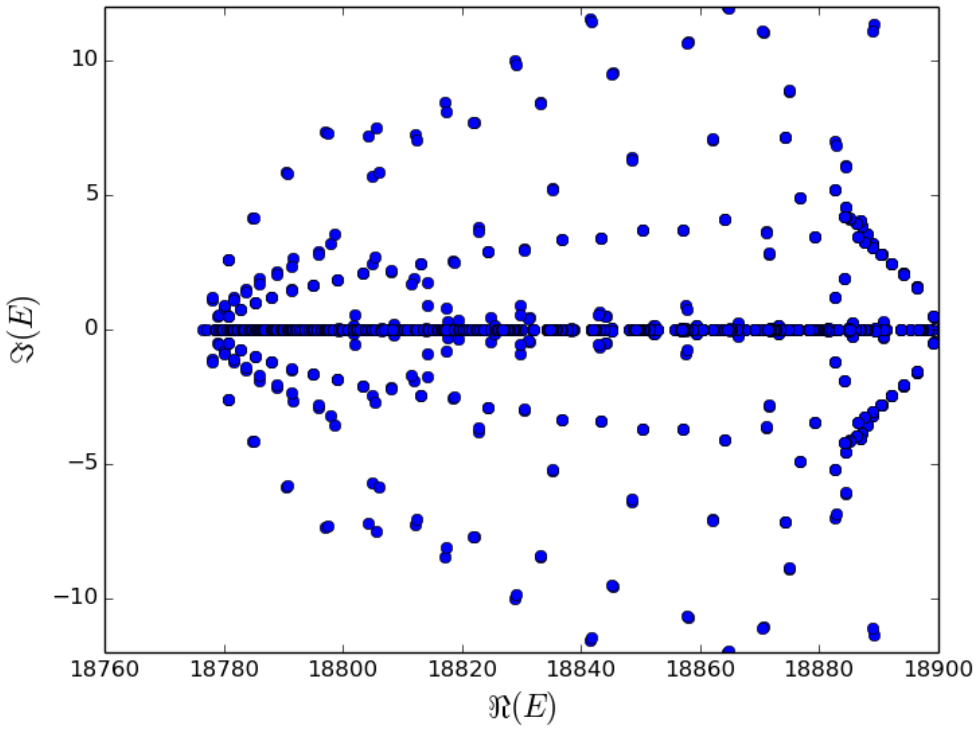

Figure 2.3: $\Re(E)$ vs $\Im(E)$ of some positive eigenvalues E, for a basis of $n = 30$ of order $k = 4$.

Table 2.2: Eigenvalues E, in atomic units, of the ground state of H_2^+ for different $\rho_{\max}$ varying the size of the basis $n = n_\rho = n_\tau$, order $k = k_\rho = k_\tau$ and $\gamma = 1/c$.

$\rho_{\max}$	$n; k$	E	$\rho_{\max}$	$n; k$	E
40	$20; 4$	17887.8	60	$20; 4$	18526.7
40	$30; 4$	17041.0	60	$30; 4$	18386.8
40	$37; 5$	16094.2	60	$37; 5$	18338.3
40	$80; 6$	15992.8	60	$80; 6$	18727.0
80	$20; 4$	18740.8	100	$20; 4$	18753.5
80	$30; 4$	18745.8	100	$30; 4$	18745.1
80	$37; 5$	18744.5	100	$37; 5$	18784.5
80	$80; 6$	18743.9	100	$80; 6$	18750.4
150	$20; 4$	18767.0	250	$20; 4$	18767.7
150	$30; 4$	18767.3	250	$30; 4$	18768.7
150	$37; 5$	18767.4	250	$37; 5$	18768.6
150	$80; 6$	18767.6	250	$80; 6$	18768.7

Table 2.3: Eigenvalues E, in atomic units, for the ground state of H_2^+ varying the dilation parameter γ using a basis of $n = 30$ B-spline functions of order $k = 4$ and $c = 137.0359895$ is the speed of light.

$\rho_{\max}$	γ	E
250	$1/c$	18774.9
250	$1/70$	18776.5
300	$1/c$	18775.5
300	$1/100$	18776.2
300	$1/70$	18776.6

the convergence. Unfortunately we cannot go beyond the basis size presented here with our currently available computer resources.

Chapter 3

Summary and outlook

We presented a systematic way of numerically calculating the ground state energy for the H_2^+ molecule, starting from *Dirac equation* and reducing it to a *generalized eigenvalue problem* to find the eigenvalues of the matrix representation of the problem using B-spline functions as basis. In the process we explored an interesting *Ansatz* that allows us to get rid of a spatial dimension of the problem considering conservation of the z-component of the total angular momentum of the electron. It was evident that the computational limitations did not allow us to approach to better results. An improvement of the convergence is expected by increasing the basis size.

We think that is important to optimize the program to a point where there is no needed so much storage capacity for the matrices and be able to get better results. Once this part is solved one might think in generalizing the idea to more complicated systems such as alkali dimers and start focusing on the *spin-orbit coupling* to understand in a more fundamental way the photo-association process, which is a very useful technique for both physicists and chemists.

Appendix A

Dirac Equation for H_2^+

In this appendix we are interested in derive the *Dirac equation* with fixed nuclei for H_2^+ in elliptic coordinates. In general form, *Dirac equation* for a stationary system reads

$$\bar{E}\bar{\phi}(\boldsymbol{r}) = [c\boldsymbol{\alpha}\cdot\boldsymbol{p} + \beta mc^2 + V(\boldsymbol{r})]\bar{\phi}(\boldsymbol{r}), \tag{A.1}$$

where $\bar{E}$ is the energy of the system, $\bar{\phi}$ is a 4-component *Dirac spinor*, $\boldsymbol{\alpha}$ and β are *Dirac matrices* and $V(x)$ is the external potential.

In matrix form this equation look like this

$$\bar{E}\begin{pmatrix}\bar{\phi}_1\\ \bar{\phi}_2\\ \bar{\phi}_3\\ \bar{\phi}_4\end{pmatrix} = \begin{pmatrix} V+mc^2 & 0 & p_z & p_x-ip_y \\ 0 & V+mc^2 & p_x+ip_y & -p_z \\ p_z & p_x-ip_y & V-mc^2 & 0 \\ p_x+ip_y & -p_z & 0 & V-mc^2 \end{pmatrix}\begin{pmatrix}\bar{\phi}_1\\ \bar{\phi}_2\\ \bar{\phi}_3\\ \bar{\phi}_4\end{pmatrix}. \tag{A.2}$$

Elliptic coordinates are defined by (A.3)

$$\rho := \frac{r_\mathrm{a}+r_\mathrm{b}}{R}, \quad \tau := \frac{r_\mathrm{a}-r_\mathrm{b}}{R}, \quad \varphi := \text{usual polar angle}, \tag{A.3}$$

where $r_{\mathrm{a,b}}$ and φ are depicted in Fig. A.1 and their relation to Cartesian coordinates are

$$x = \frac{R}{2}\cos\varphi\sqrt{(\rho^2-1)(1-\tau^2)}, \quad y = \frac{R}{2}\sin\varphi\sqrt{(\rho^2-1)(1-\tau^2)}, \quad z = -\frac{R\rho\tau}{2}. \tag{A.4}$$

The ranges of these new variables are $1 \le \rho < \infty$, $-1 \le \tau \le 1$ and $0 < \varphi \le 2\pi$.

It is also important to know the explicit form of each component of the momentum operator $\boldsymbol{p} = (p_x, p_y, p_z)$ as a function of ρ, τ and φ. As $\boldsymbol{p} = -i\hbar\sum_j \frac{\boldsymbol{e}_j}{h_j}\frac{\partial}{\partial x_j}$, where $\boldsymbol{e}_j$ and h_j are the unitary vector and the *Lamé coefficient* in the x_j direction respectively, we have

$$p_x = \frac{2\hbar}{iR}\left[\frac{[(\rho^2-1)(1-\tau^2)]^{1/2}}{\rho^2-\tau^2}\cos\varphi\left(\rho\frac{\partial}{\partial\rho} - \tau\frac{\partial}{\partial\tau}\right) + \frac{-\sin\varphi}{[(\rho^2-1)(1-\tau^2)]^{1/2}}\frac{\partial}{\partial\varphi}\right], \tag{A.5}$$

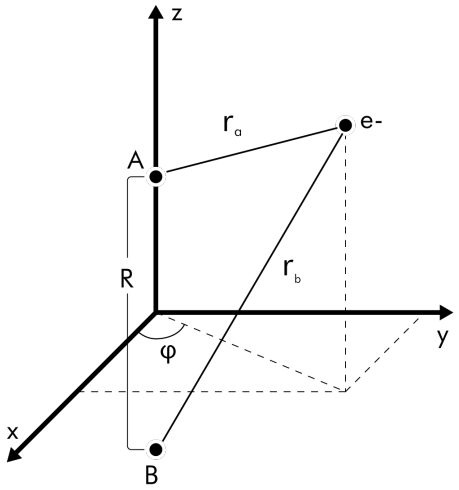

Figure A.1: diagram for H_2^+ molecule, nuclei A and B lay on z-axis

$$p_y = \frac{2\hbar}{iR}\left[\frac{[(\rho^2-1)(1-\tau^2)]^{1/2}}{\rho^2-\tau^2}\sin\varphi\left(\rho\frac{\partial}{\partial\rho}-\tau\frac{\partial}{\partial\tau}\right)+\frac{\cos\varphi}{[(\rho^2-1)(1-\tau^2)]^{1/2}}\frac{\partial}{\partial\varphi}\right], \tag{A.6}$$

$$p_z = \frac{2\hbar}{iR}\frac{1}{\rho^2-\tau^2}\left[(1-\rho^2)\tau\frac{\partial}{\partial\rho}+(\tau^2-1)\rho\frac{\partial}{\partial\tau}\right], \tag{A.7}$$

and the potential

$$V(\rho,\tau) = \frac{Ze^2}{R}\left(\frac{-4\rho}{\rho^2-\tau^2}\right). \tag{A.8}$$

Using (A.2),(A.5-A.8) it is posible to write the equation for every component of the *Dirac spinor*

$$\begin{aligned}\bar{E}\bar{\phi}_1 = &\left[\frac{Ze^2}{R}\left(\frac{-4\rho}{\rho^2-\tau^2}\right)+mc^2)\right]\bar{\phi}_1+\frac{2\hbar}{iR}\left[\frac{1}{\rho^2-\tau^2}\left[(1-\rho^2)\tau\frac{\partial}{\partial\rho}+(\tau^2-1)\rho\frac{\partial}{\partial\tau}\right]\right]\bar{\phi}_3\\ &+\frac{2\hbar}{R}e^{-i\varphi}\left[\frac{-1}{[(\rho^2-1)(1-\tau^2)]^{1/2}}\frac{\partial}{\partial\varphi}-i\left[\frac{[(\rho^2-1)(1-\tau^2)]^{1/2}}{\rho^2-\tau^2}\left(\rho\frac{\partial}{\partial\rho}-\tau\frac{\partial}{\partial\tau}\right)\right]\right]\bar{\phi}_4,\end{aligned} \tag{A.9}$$

$$\begin{aligned}\bar{E}\bar{\phi}_2 = &\left[\frac{Ze^2}{R}\left(\frac{-4\rho}{\rho^2-\tau^2}\right)+mc^2)\right]\bar{\phi}_2-\frac{2\hbar}{iR}\left[\frac{1}{\rho^2-\tau^2}\left[(1-\rho^2)\tau\frac{\partial}{\partial\rho}+(\tau^2-1)\rho\frac{\partial}{\partial\tau}\right]\right]\bar{\phi}_4\\ &-\frac{2\hbar}{R}e^{i\varphi}\left[\frac{-1}{[(\rho^2-1)(1-\tau^2)]^{1/2}}\frac{\partial}{\partial\varphi}+i\left[\frac{[(\rho^2-1)(1-\tau^2)]^{1/2}}{\rho^2-\tau^2}\left(\rho\frac{\partial}{\partial\rho}-\tau\frac{\partial}{\partial\tau}\right)\right]\right]\bar{\phi}_3,\end{aligned} \tag{A.10}$$

$$\bar{E}\bar{\phi}_3 = \left[\frac{Ze^2}{R}\left(\frac{-4\rho}{\rho^2-\tau^2}\right) - mc^2)\right]\bar{\phi}_3 + \frac{2\hbar}{iR}\left[\frac{1}{\rho^2-\tau^2}\left[(1-\rho^2)\tau\frac{\partial}{\partial\rho} + (\tau^2-1)\rho\frac{\partial}{\partial\tau}\right]\right]\bar{\phi}_1$$
$$+ \frac{2\hbar}{R}e^{-i\varphi}\left[\frac{-1}{[(\rho^2-1)(1-\tau^2)]^{1/2}}\frac{\partial}{\partial\varphi} - i\left[\frac{[(\rho^2-1)(1-\tau^2)]^{1/2}}{\rho^2-\tau^2}\left(\rho\frac{\partial}{\partial\rho} - \tau\frac{\partial}{\partial\tau}\right)\right]\right]\bar{\phi}_2, \quad \text{(A.11)}$$

$$\bar{E}\bar{\phi}_4 = \left[\frac{Ze^2}{R}\left(\frac{-4\rho}{\rho^2-\tau^2}\right) - mc^2)\right]\bar{\phi}_4 - \frac{2\hbar}{iR}\left[\frac{1}{\rho^2-\tau^2}\left[(1-\rho^2)\tau\frac{\partial}{\partial\rho} + (\tau^2-1)\rho\frac{\partial}{\partial\tau}\right]\right]\bar{\phi}_2$$
$$- \frac{2\hbar}{R}e^{-i\varphi}\left[\frac{-1}{[(\rho^2-1)(1-\tau^2)]^{1/2}}\frac{\partial}{\partial\varphi} + i\left[\frac{[(\rho^2-1)(1-\tau^2)]^{1/2}}{\rho^2-\tau^2}\left(\rho\frac{\partial}{\partial\rho} - \tau\frac{\partial}{\partial\tau}\right)\right]\right]\bar{\phi}_1, \quad \text{(A.12)}$$

What we can see form this system of equations is that the coordinate φ couples just $\bar{\phi}_1$ with $\bar{\phi}_3$ and $\bar{\phi}_2$ with $\bar{\phi}_4$, so we can use the following *Ansatz*

$$\bar{\phi}_k(\rho,\tau,\varphi) = \phi_k(\rho,\tau)e^{i(\mu-1/2+\lambda_k)\varphi} \quad \text{(A.13)}$$

where the parameter $\lambda_k = (0,1,0,1)$ for $k = (1,2,3,4)$. Using this *Ansatz* we can eliminate the coordinate φ from our equations and we get a two-dimensional system of four differential equations

$$\bar{E}\phi_1 = \left[\frac{Ze^2}{R}\left(\frac{-4\rho}{\rho^2-\tau^2}\right) + mc^2)\right]\phi_1 - i\frac{2\hbar}{R}\left[\frac{1}{\rho^2-\tau^2}\left[(1-\rho^2)\tau\frac{\partial}{\partial\rho} + (\tau^2-1)\rho\frac{\partial}{\partial\tau}\right]\right]\phi_3$$
$$+ i\frac{2\hbar}{R}\left[\frac{\mu+1/2}{[(\rho^2-1)(1-\tau^2)]^{1/2}} - \frac{[(\rho^2-1)(1-\tau^2)]^{1/2}}{\rho^2-\tau^2}\left(\rho\frac{\partial}{\partial\rho} - \tau\frac{\partial}{\partial\tau}\right)\right]\phi_4, \quad \text{(A.14)}$$

$$\bar{E}\phi_2 = \left[\frac{Ze^2}{R}\left(\frac{-4\rho}{\rho^2-\tau^2}\right) + mc^2)\right]\phi_2 + i\frac{2\hbar}{R}\left[\frac{1}{\rho^2-\tau^2}\left[(1-\rho^2)\tau\frac{\partial}{\partial\rho} + (\tau^2-1)\rho\frac{\partial}{\partial\tau}\right]\right]\phi_4$$
$$+ i\frac{2\hbar}{R}\left[-\frac{\mu-1/2}{[(\rho^2-1)(1-\tau^2)]^{1/2}} - \frac{[(\rho^2-1)(1-\tau^2)]^{1/2}}{\rho^2-\tau^2}\left(\rho\frac{\partial}{\partial\rho} - \tau\frac{\partial}{\partial\tau}\right)\right]\phi_3, \quad \text{(A.15)}$$

$$\bar{E}\phi_3 = \left[\frac{Ze^2}{R}\left(\frac{-4\rho}{\rho^2-\tau^2}\right) - mc^2)\right]\phi_3 - i\frac{2\hbar}{R}\left[\frac{1}{\rho^2-\tau^2}\left[(1-\rho^2)\tau\frac{\partial}{\partial\rho} + (\tau^2-1)\rho\frac{\partial}{\partial\tau}\right]\right]\phi_1$$
$$+ i\frac{2\hbar}{R}\left[\frac{\mu+1/2}{[(\rho^2-1)(1-\tau^2)]^{1/2}} - \frac{[(\rho^2-1)(1-\tau^2)]^{1/2}}{\rho^2-\tau^2}\left(\rho\frac{\partial}{\partial\rho} - \tau\frac{\partial}{\partial\tau}\right)\right]\phi_2, \quad \text{(A.16)}$$

$$\bar{E}\phi_4 = \left[\frac{Ze^2}{R}\left(\frac{-4\rho}{\rho^2-\tau^2}\right) - mc^2)\right]\phi_4 + i\frac{2\hbar}{R}\left[\frac{1}{\rho^2-\tau^2}\left[(1-\rho^2)\tau\frac{\partial}{\partial\rho} + (\tau^2-1)\rho\frac{\partial}{\partial\tau}\right]\right]\phi_2$$
$$+ i\frac{2\hbar}{R}\left[-\frac{\mu-1/2}{[(\rho^2-1)(1-\tau^2)]^{1/2}} - \frac{[(\rho^2-1)(1-\tau^2)]^{1/2}}{\rho^2-\tau^2}\left(\rho\frac{\partial}{\partial\rho} - \tau\frac{\partial}{\partial\tau}\right)\right]\phi_1. \quad \text{(A.17)}$$

As we can see we might have some troubles when the denominators $(\rho^2-1)(1-\tau^2)$ and $[(\rho^2-1)(1-\tau^2)]^{1/2}$ are zero; these points are actually the positions of the nuclei: $(\rho,\tau)=(1,1)$ for nucleus B and $(\rho,\tau)=(1,-1)$ for nucleus A so these problems can be avoided by imposing boundary conditions but anyhow numerically we need to lift these divergences, to do that we define the following quantities

$$\bar{A}_\pm := \left[\frac{Ze^2}{R}\left(\frac{-4\rho}{\rho^2-\tau^2}\right)\pm mc^2)\right], \quad \bar{B} := -i\frac{2\hbar}{R}\frac{1}{\rho^2-\tau^2}\left[(1-\rho^2)\tau\frac{\partial}{\partial\rho}+(\tau^2-1)\rho\frac{\partial}{\partial\tau}\right],$$
$$\bar{C}_\pm := i\frac{2\hbar}{R}\left[\frac{(\mu\pm 1/2)}{[(\rho^2-1)(1-\tau^2)]^{1/2}}-\frac{[(\rho^2-1)(1-\tau^2)]^{1/2}}{\rho^2-\tau^2}\left(\rho\frac{\partial}{\partial\rho}-\tau\frac{\partial}{\partial\tau}\right)\right], \quad \bar{D} := [(\rho^2-1)(1-\tau^2)]^{1/2}(\rho^2-\tau^2), \tag{A.18}$$

and we multiply (A.14)-(A.17) by $\bar{D}$ getting the system

$$\bar{D}\bar{E}\phi_1 = \bar{D}(\bar{A}_+\phi_1+\bar{B}\phi_3+\bar{C}_+\phi_4) \tag{A.19}$$

$$\bar{D}\bar{E}\phi_2 = \bar{D}(\bar{A}_+\phi_2-\bar{B}\phi_4+\bar{C}_-\phi_3) \tag{A.20}$$

$$\bar{D}\bar{E}\phi_3 = \bar{D}(\bar{A}_-\phi_3+\bar{B}\phi_1+\bar{C}_+\phi_2) \tag{A.21}$$

$$\bar{D}\bar{E}\phi_4 = \bar{D}(\bar{A}_-\phi_4-\bar{B}\phi_2+\bar{C}_-\phi_1) \tag{A.22}$$

Using the convention $X=\bar{D}\bar{X}$ for $\bar{X}=\bar{A}_\pm,\bar{B},\bar{C}_\pm,\bar{E}$ we can write our problem in matrix form

$$E\begin{pmatrix}\phi_1\\ \phi_2\\ \phi_3\\ \phi_4\end{pmatrix} = \begin{pmatrix}A_+ & 0 & B & C_+\\ 0 & A_+ & C_- & B^*\\ B & C_+ & A_- & 0\\ C_- & B^* & 0 & A_-\end{pmatrix}\begin{pmatrix}\phi_1\\ \phi_2\\ \phi_3\\ \phi_4\end{pmatrix} \tag{A.23}$$

which is an *eigenvalue problem*.

Bibliography

[1] Juris Ulmanis, Johannes Deiglmayr, Marc Repp, Roland Wester, and Matthias Weidemuller. *Ultracold molecules formed by photoassociation: Heteronuclear dimers, inelastic collisions, and interactions with ultrashort laser pulses*. *Chemical Reviews* **112**(9), 4890–4927 (2012). DOI: 10.1021/cr300215h.

[2] Christiane P. Koch and Moshe Shapiro. *Coherent Control of Ultracold Photoassociation*. *Chemical Reviews* **112**(9), 4928–4948 (2012). DOI: 10.1021/cr2003882.

[3] B. E. Londoño, J. E. Mahecha, E. Luc-Koenig, and A. Crubellier. *Resonant coupling effects on the photoassociation of ultracold Rb and Cs atoms*. *Physical Review A* **80**(3), 032511 (2009). DOI: 10.1103/PhysRevA.80.032511.

[4] W. C. Stwalley, J. Banerjee, M. Bellos, R. Carollo, M. Recore, and M. Mastroianni. *Resonant Coupling in the Heteronuclear Alkali Dimers for Direct Photoassociative Formation of X(0,0) Ultracold Molecules*. *The Journal of Physical Chemistry A* **114**(1), 81–86 (2010). DOI: 10.1021/jp901803f.

[5] H. Salami, T. Bergeman, B. Beser, J. Bai, E. H. Ahmed, S. Kotochigova, A. M. Lyyra, J. Huennekens, C. Lisdat, A. V. Stolyarov, O. Dulieu, P. Crozet, and A. J. Ross. *Spectroscopic observations, spin-orbit functions, and coupled-channel deperturbation analysis of data on the A* Σ *1 u + and b* Π *3 u states of Rb 2*. *Physical Review A* **80**(2), 022515 (2009). DOI: 10.1103/PhysRevA.80.022515.

[6] Jean Mawhin and André Ronveaux. *Schrödinger and Dirac equations for the hydrogen atom, and Laguerre polynomials*. *Archive for History of Exact Sciences* **64**(4), 429–460 (2010). DOI: 10.1007/s00407-010-0060-3.

[7] DAVID EDVARDSSON, STEN LUNELL, and CHRISTEL M. MARIAN. *Calculation of potential energy curves for Rb 2 including relativistic effects*. *Molecular Physics* **101**(15), 2381–2389 (2003). DOI: 10.1080/0026897031000121307.

[8] I. J. Schoenberg. *Contributions to the Problem of Approximation of Equidistant Data by Analytic Functions*. In *I. J. Schoenberg Selected Papers*, pages 3–57. Birkhäuser Boston, Boston, MA (1988).

[9] Carlos Mario Granados-Castro. *Time-Dependent Feshbach Method for the Dynamical Study of Photoionization and Autoionization in Two-Electron Atomic Systems*. (2012).

[10] Bruce W. Shore. *Solving the radial Schrodinger equation by using cubic-spline basis functions*. *The Journal of Chemical Physics* **58**(9), 3855 (1973). DOI: 10.1063/1.1679740.

[11] B W Shore, Fernbach S Alder B, Rotenberg M (eds), Bain R A N, Bardsley J, Zel'dovich Ya B Baz' A I, Perelomov A M, Blatt J M F, Weiskopf V, Bloch C, Brenig W R, Haag, Hibbert A Burke P G, Robb W D, Burke P G D, Robb W, Burke P G J, Seaton M, Chung K T Chen J C Y, Sinfailam A-L, Courant R D, Hilbert, Eu B C J, Ross, Fano U, Fels M F W, Hazi A, Feshbach H, Foldy L L D, Waleka J, Fox L, Garside L W, Tobocman, Gear C W, Gottfried K, Haglund M E D, Robson, Ham F S, Harris F E, Hazi A W S, Taylor H, Heller E J, Hodgson P G, Humblet J, Humblet J L, Rosenfeld, Jackson J L E, Wyatt R, Balint-Kurti G G Johnson B R, Levine R D, Lambert J D, Lane A M G, Thomas R, Levinson N, Mahaux C A, Weidenmüller H, Matese J J W, Henry R J, Mikhlin S G, Mikhlin S G L, Smolitskiy K, Mott N F W, Massey H S, Newton R, Oberoi R S K, Nesbet R, Oberoi R S K, Nesbet R, Percival I, Risberg V, Seaton M J, Seaton M J, Shore B W, Shore B W, Smith K, Stetter H J, Taylor H S, Truhlar D G, Truhlar D G, and Wolken G Jr. *Use of boundary-condition wavefunctions for bound states, continuum states, and resonances*. *Journal of Physics B: Atomic and Molecular Physics* **7**(18), 2502–2517 (1974). DOI: 10.1088/0022-3700/7/18/015.

[12] W. R. Johnson, S. A. Blundell, and J. Sapirstein. *Finite basis sets for the Dirac equation constructed from B splines*. *Physical Review A* **37**(2), 307–315 (1988). DOI: 10.1103/PhysRevA.37.307.

[13] M. H. Chen, K. T. Cheng, and W. R. Johnson. *Relativistic configuration-interaction calculations of n =2 triplet states of heliumlike ions*. *Physical Review A* **47**(5), 3692–3703 (1993). DOI: 10.1103/PhysRevA.47.3692.

[14] Bernd Thaller. *The Dirac Equation*. Springer Berlin Heidelberg, Berlin, Heidelberg (1992).

[15] Franz Schwabl. *Advanced Quantum Mechanics*. Springer Berlin Heidelberg, Berlin, Heidelberg (2008).

[16] G. B. Deineka. *Dirac-Fock calculation for H, H2+ and H2 in a strong magnetic field by the Hermitian basis of B-splines*. , 1–22 (1999).

[17] Carl. De Boor. *A practical guide to splines : with 32 figures*. Springer (2001).

[18] H Bachau, E Cormier, P Decleva, J E Hansen, and F Martín. *Applications of B -splines in atomic and molecular physics*. *Reports on Progress in Physics* **64**(12), 1815–1943 (2001). DOI: 10.1088/0034-4885/64/12/205.

[19] Cornelius Lanczos. *An iterative method for the solution of the eigenvalue problem of linear differential and integral*. *Journal of Research of the National Bureau of Standards Section B* **45**(225) (1950).

[20] B. N. Parlett, D. S. Scott, Chandler Davis, W. M. Kahan, W. Kahan, B. N. Parlett, Shmuel Kaniel, Cornelius Lanczos, C. C. Paige, and C. C. Paige. *The Lanczos algorithm with selective orthogonalization*. *Mathematics of Computation* **33**(145), 217–238 (1979). DOI: 10.1090/S0025-5718-1979-0514820-3.

[21] Thomas Ericsson, Axel Ruhe, J. H. Argyris, Th. L. Johnsen, R. A. Rosanoff, J. R. Roy, James R. Bunch, Linda Kaufman, J. Alan George, Paul S. Jensen, C. C. Paige, C. C. Paige, Beresford N. Parlett, B. N. Parlett, D. S. Scott, Axel Ruhe, Gilbert Strang, and George J. Fix. *The spectral transformation Lánczos method for the numerical solution of large sparse generalized symmetric eigenvalue problems*. *Mathematics of Computation* **35**(152), 1251–1251 (1980). DOI: 10.1090/S0025-5718-1980-0583502-2.

[22] Andreas Krug. *Alkali Rydberg States in Electromagnetic Fields*. (2001).

[23] Edward R. Vrscay. *Hydrogen atom with a Yukawa potential: Perturbation theory and continued-fractions – Padé approximants at large order*. *Physical Review A* **33**(2), 1433–1436 (1986). DOI: 10.1103/PhysRevA.33.1433.

[24] Javier Madronero. *Spectral properties of planar helium under periodic driving* (2004).

[25] Atsushi Ishikawa, Hiroyuki Nakashima, and Hiroshi Nakatsuji. *Solving the Schrödinger and Dirac equations of hydrogen molecular ion accurately by the free iterative complement interaction method*. *Journal of Chemical Physics* **128**(12), 1–13 (2008). DOI: 10.1063/1.2842068.

[26] Hiroyuki Nakashima and Hiroshi Nakatsuji. *Non-Born-Oppenheimer potential energy curve: Hydrogen molecular ion with highly accurate free complement method*. *Journal of Chemical Physics* **139**(7), 1–10 (2013). DOI: 10.1063/1.4818161.